Development of Chemical Treatment Alternatives for Tetraphenylborate Destruction in Tank 48H

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#### **Abstract:**

This study assessed chemical treatment options for decomposing the tetraphenylborate in High Level Waste (HLW) Tank 48H. Tank 48H, located at the Savannah River Site in Aiken, SC, contains approximately one million liters of HLW. The tetraphenylborate slurry represents legacy material from commissioning of an In Tank Precipitation process to separate radioactive cesium and actinides from the nonradioactive chemicals. During early operations, the process encountered an unplanned chemical reaction that catalytically decomposed the excess tetraphenylborate producing benzene. Subsequent research indicated that personnel could not control the operations within the existing equipment to both meet the desired treatment rate for the waste and maintain the benzene concentration within allowable concentrations. Since then, the Department of Energy selected an alternate treatment process for handling high-level waste at the site. However, the site must destroy the tetraphenylborate before returning the tank to HLW service.

The research focuses on identifying treatments to decompose tetraphenylborate to the maximum extent feasible, with a preference for decomposition methods that produce carbon dioxide rather than benzene. A number of experiments examined whether the use of oxidants, catalysts or acids proved effective in decomposing the tetraphenylborate. Additional experiments developed an understanding of the solid, liquid and gas decomposition products. The testing identified several successful treatment options including:

- an iron catalyst combined with hydrogen peroxide (Fenton's reagent) with added acid,
- sodium permanganate with added acid, and
- copper catalyst with added acid.

#### **Screening Experiments**

We completed a series of tests to evaluate the Tank 48H Team's alternatives and to develop additional alternatives for consideration. The experimental design allowed direct comparison of the various chemical treatment options under comparable conditions. The bulk of the tests examined the destruction efficiency at 7 days for different chemical recipes with a subset of the tests aimed at determining the influence of temperature and the stoichiometry of the reactions (i.e., amount destroyed as a function of the amount of reagent added). A final set of experiments collected and analyzed samples of the slurry and the offgas as a function of time in an attempt to complete a carbon balance for several of the most promising decomposition options.

Analyzing the filtrate for soluble potassium and boron provided indirect measure of the degree of tetraphenylborate (TPB) decomposition. As the TPB decomposes, the byproducts become soluble and the soluble potassium and boron increase. In comparing the alternatives, we present graphs showing the percent TPB destruction based on the increase in soluble potassium and boron concentration. The soluble potassium is more accurate than soluble boron for the prediction of TPB decomposition since insoluble boron compounds form during decomposition, especially under acidic conditions.

Testing used either unwashed or washed precipitate. It would be preferable for the process to treat unwashed precipitate as this would simplify processing and minimize additional waste generation through processing. The current Tank 48H contents are unwashed and contain a high concentration of sodium hydroxide, sodium nitrate and sodium nitrite. Historical processing required washing of the precipitate slurry to remove the nonradioactive salts for subsequent processing by the Saltstone Facility. This washing reduced the concentration of sodium to 0.13 M and the nitrite from 0.47 M to 0.01 M. This degree of washing assumes pretreatment of the contents of Tank 48H by addition of 7.6 million liters (2 million gallons) of inhibited water (i.e., 0.01 M NaOH) and filtration to remove the excess volume (6.62 million liters or 1.75 million gallons). Washing would most likely need to occur in Tank 48H using the Building 241-96H filters. The wash water will require evaporation or disposal through the Saltstone facility.

It should be noted that percent destruction means that the cesium and potassium are being released into solution although the decomposition of the TPB to benzene or CO<sub>2</sub> may not be complete. As a result, additional analysis of the organic present for the options with high destruction rates determined the degree of decomposition for the organic.

In addition, personnel measured the solution pH after each 7-day test and twice per day in the final set of tests. The solution pH is especially important in the tests that may be processed in-tank. Attempts were made to complete some of the tests at pH 9.5. However, due to the over addition of acid in the experiments, the final solution pH proved lower than planned.

#### **Catalytic Options**

A number of catalytic options were proposed to destroy the TPB in Tank 48H. This is because of the success of the copper catalyzed acid hydrolysis process used in the Defense Waste Processing Facility or DWPF (Marra, et al. 1996) <sup>1</sup> chemical commissioning and the successful use of the copper catalyst to destroy TPB in Tank 49H (Peters, 2001). However, the destruction of the TPB in Tank 48H is expected to be much more difficult than Tank 49H due to the higher concentration of TPB and the insolubility of the KTPB and CsTPB. (Tank 49H contained primarily soluble NaTPB)

Catalyst testing considered four catalysts based on previous catalyst testing: copper, palladium, platinum and iron. Copper and palladium have been used at SRS to decompose TPB. Platinum was chosen due to its good catalytic activity in similar chemistry. Iron was chosen due to its ability to catalyze peroxide through Fenton's chemistry. The catalysts were tested at 25 °C and 40 °C.

## Feed KTPB Slurry to DWPF Salt Cell for Catalytic Decomposition

# Catalytic Decomposition of TPB in a New or Existing Facility

Both of the above processes use a copper catalyzed, formic acid hydrolysis reaction to destroy the TPB. This process was used in DWPF during chemical commissioning. No testing was completed to duplicate this processing, as this is a very mature technology (Lambert et al., 1998). However, several tests were completed at similar processing conditions. These tests used 1000 ppm Cu with added formic acid using a washed precipitate. These tests resulted in 80% and 100% destruction of the TPB at 25 °C and 40 °C, respectively.

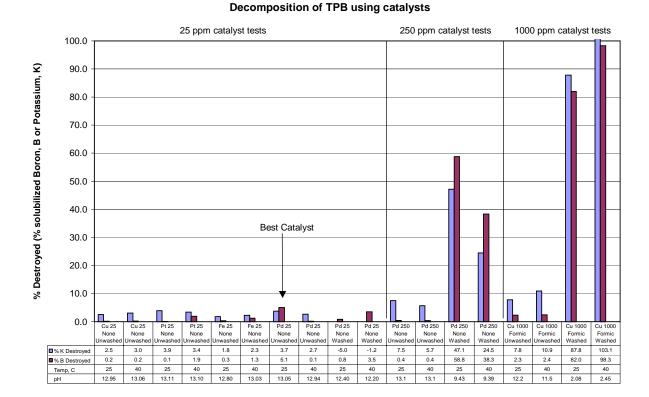
<sup>&</sup>lt;sup>1</sup> DWPF is the nation's largest glassification plant. We vitrify (change to glass) the approximate 35 million gallons of liquid radioactive waste by-product that has accumulated at SRS since the early 1950s. Vitrifying the waste resolves the problem of safe, long-term storage of the material.

#### Catalytic Decomposition of TPB Directly in Tank 48H

Several of the experiments examined whether it would be feasible to add a catalyst to Tank 48H to complete the destruction of TPB in the tank. Catalytic decomposition is likely to lead to a large production of benzene. Figure 1 shows that the catalysts tested had low TPB destruction rates with added catalyst concentration of 25 mg catalyst per kg of slurry.

Because of the low TPB destruction during the seven days of testing at 25 mg/kg, personnel conducted additional tests at higher catalyst concentrations. The testing conditions chosen were 250 mg/kg palladium and 1000 mg/kg copper. These concentrations were chosen, as these were the maximum concentrations tested by other researchers. In testing at higher catalyst concentrations, the catalysts proved most effective in the washed simulate. The destruction rate increased approximately six-fold with the palladium catalyst and roughly ten-fold with the copper catalyst.

The TPB destruction rate of the catalysts in the unwashed precipitate was much less effective than in the washed precipitate. In testing with the washed precipitate, increasing the palladium concentration tenfold led to a ten-fold increase in TPB destruction. However, in testing the unwashed precipitate, increasing the palladium concentration ten-fold led to just a two-fold increase in TPB destruction. The use of a catalyst in-tank (unwashed precipitate) might be effective, but would have a slower destruction rate than many of the other alternatives. If the development of an in-tank alternative is desirable, consideration should be given to testing the Pd catalyst at 250 – 1000 ppm in experiments with unwashed precipitate for longer time periods (continue testing for several months) to determine the time necessary to completely destroy the TPB.



#### Figure 1 - Comparison of Catalysts for TPB Destruction

# Catalytic Decomposition of TPB Directly in Tank by Lowering pH (Acid Addition)

We examined whether the combination of catalyst and acid would lead to rapid TPB decomposition. Formic acid and 1000 ppm of copper catalyst were added to each of these experiments. The results are summarized in the last four columns of Figure 1. Copper proved much less effective in destroying TPB in unwashed precipitate. However, the TPB rapidly decomposed in experiments with washed precipitate. Since the tanks are fabricated from carbon steel, this process is not a viable in-tank due to the pH being too low.

# Catalytically Decompose TPB Using Tank 49H as a Reaction Vessel

This option would feed the contents of Tank 48H to Tank 49H where the decomposition would take place.

A catalyst would be present in Tank 49H to decompose the TPB. Tank 49H would be suitable for this service since it was modified to allow the use of nitrogen to inert the tank and prevent a flammable mixture from

forming during processing. This has some advantages over catalytic destruction in Tank 48H as the precipitate volume can be controlled.

There are some disadvantages to this option including the fact that it would tie up an additional tank throughout the duration of the processing. Tank 49H has been returned to service as a high level waste tank and is not currently available for this service. This is a more controlled reaction than completing the decomposition in Tank 48H because it would be possible to control the slurry volume fed to the reaction vessel. However, it requires an additional waste tank and is impractical at this time.

This was considered as one of several options for catalytic destruction of the TPB. This could be accomplished for catalytic destruction of the TPB in a new tank, in an existing tank or in a processing vessel inside the tank.

# Volume-Reduce by Filtration, Sending Filtrate to Tank 50H, Catalytic Decomposition of Residual In-Tank

This option is similar to the above option but also requires the startup and operation of the Building 241-96H filters to concentrate the waste. Current plans call for this equipment to be used as part of the Actinide Removal Process<sup>2</sup>. As was noted previously, the use of a catalyst by itself is unlikely to be effective. This option was not evaluated independent of catalytic destruction inside Tank 48H by the Team.

# **Thermal Options**

A number of thermal conditions were explored to determine the impact of temperature on TPB decomposition. Based on previous experience with TPB, higher temperature was expected to have a strong impact on TPB decomposition. The Salt Cell Process destroys the TPB by hydrolyzing the TPB to benzene at 90 °C. Testing was planned at 25 °C and 40 °C, as these are the typical ranges for in-tank processes, and at 90 °C as this temperature exceeds benzene's boiling point. Other thermal options such as steam reforming would be processed at much higher temperatures.

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<sup>&</sup>lt;sup>2</sup> The actinide removal process is a new process that is designed to remove Actinides (Uranium, Plutonium) and Strontium from Salt Waste at SRS.

Testing was performed at room temperature (~25 °C), 40 °C, and 90 °C. For most of the testing with catalyst, acids and oxidants, higher temperatures led to more complete destruction of TPB. The exception was that the palladium catalyst led to lower destruction at higher temperatures, which defies expectations from prior studies. Most likely, the difference either reflects a variance in the inducting period for the Pd between the two experiments or some other uncontrolled variable that altered the activity of the added Pd. Below is an evaluation of the thermal treatment options. Figure 2 is a comparison of TPB destruction at various temperatures.

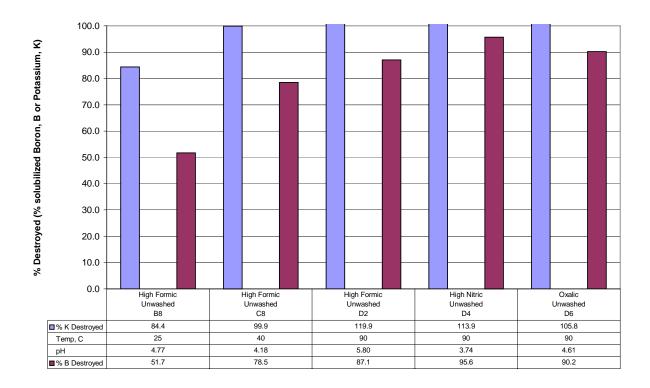


Figure 2- Comparison of Catalysts for TPB Destruction

### Thermal Decomposition of TPB

The TPB will decompose under extreme conditions of temperature and pressure. Previous thermogravimetric testing measured the TPB auto-ignition temperature of ~325 °C. <sup>5</sup> For that reason, thermal (i.e., high temperature) and steam reforming (600-800 °C) processes are very likely to result in TPB decomposition. However, these processes would not be deployable as in-tank processes. Steam reforming has the added advantage that control of the oxidizing conditions in the column would lead to conversion of nitrite and nitrate to nitrogen and conversion of TPB to carbon dioxide.

### **Oxidation Options**

Four oxidants – sodium permanganate (NaMnO<sub>4</sub>), hydrogen peroxide ( $H_2O_2$ ), sodium perborate (NaBO<sub>3</sub>) and potassium ferrate ( $K_2FeO_4$ ) – were tested to determine the best oxidant for destruction of TPB. Because of difficulty finding a commercial source of potassium ferrate, only two ferrate experiments were performed using an old and suspect sample of the reagent.

The use of an oxidant may lead to lower benzene production and high generation of carbon dioxide and other decomposition products that are less flammable than benzene. Sodium permanganate was the best oxidant in our testing. Testing was completed at oxidant levels of two (i.e., low) and five (i.e., high) moles of oxidant per mole of TPB. The most complete destruction of TPB (25%) occurred at 40 °C, so there is a definite advantage at this higher temperature. The TPB decomposition was more complete with washed precipitate, but that may be due to the lower pH of the washed precipitate as testing of permanganate plus formic acid also led to a higher TPB destruction. The results of these experiments are summarized in Figure 3.

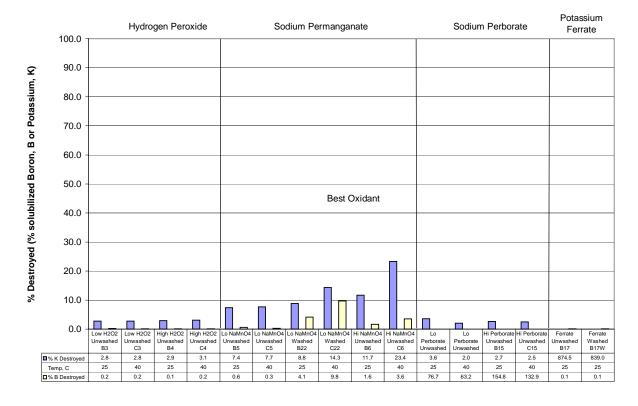


Figure 3 -- Comparison of Oxidants for Destruction of TPB

# Actinide Removal Process (ARP) Oxidation of TPB Using Permanganate

#### Oxidation of TPB Using Permanganate

These two options used permanganate as an oxidant to destroy TPB. The first option above, the oxidation of TPB in the Actinide Removal Facility, is an out of tank alternative to the second option, the Oxidation of TPB In-tank.

The experiments using sodium permanganate led to the destruction of 7% to 23% of the TPB as measured by the increase in soluble potassium. Figure 3 summarizes the results of the various oxidants tested. As can be seen from Figure 3, sodium permanganate was the best oxidant tested. It should also be noted that the TPB destruction was more complete at 40 °C than at 25 °C. The last fact to be noted from this testing is that the higher addition of sodium permanganate (5 moles of oxidant per mole of TPB) led to a significantly higher TPB destruction than the lower addition of sodium permanganate (2 moles of oxidant per mole of TPB).

A carbon mass balance was performed to understand the degree of TPB decomposition and the byproducts that formed during decomposition. The simple TPB decomposition products for hydrolysis are (oxidation and other competing reactions are more complex):

Na 
$$(C_6H_5)_4$$
 (TPB or  $4PB^3$ )  $\rightarrow 3PB + Benzene$  [1]  
 $3PB \rightarrow 2PB + Benzene$  [2]  
 $2PB \rightarrow 1PB + Benzene$  [3]

1PB → Boric Acid + Benzene [4]

Analysis of the decomposition products from the experiment using 5 moles permanganate per mole of TPB based on HPLC analysis showed that 11.7% of the TPB decomposed, primarily to 3PB and 2PB. Based on the carbon balance, 4.8% of the original organic carbon was converted to 3PB and 4.2% of the original organic carbon was converted to 2PB. Phenol, 1PB and other decomposition products accounted for <1% of the decomposition products. If the TPB decomposed to form benzene along with the 2PB and 3PB, we calculated that 3.7% of the original organic carbon would be present as benzene. Summing these

decomposition products (3PB + 2PB + benzene) should equal the amount of TPB decomposed. This sum is 12.7%, which agrees well with the 11.7% decomposition predicted by the HPLC analyses. Note that this is a much lower decomposition than was predicted by the soluble potassium analysis (23% decomposition predicted by soluble K. The agreement between soluble K and TPB destruction by HPLC was excellent in the other experiments where both analyses were performed.

The disadvantage of using NaMnO<sub>4</sub> is that it will result in the addition of MnO<sub>2</sub>, an insoluble oxide in HLW. The quantity of MnO<sub>2</sub> that would result from the addition of five moles of NaMnO<sub>4</sub> per mole of TPB (57,600 kg or 127,000 lb) equates to the addition of 32,000 kg or 70,500 lb of MnO<sub>2</sub> to the HLW. This is equivalent to the Mn present in 1.59 million liters (600,000 gallons) of sludge. Linear extrapolation of the data suggests that it does not seem feasible to destroy the TPB with permanganate by itself without the addition of a huge quantity of NaMnO<sub>4</sub> such as 21.7 moles of NaMnO<sub>4</sub> per mole of TPB (250,000 kg or 560,000 lb of NaMnO<sub>4</sub>).

#### Oxidation of TPB Using Water Soluble Mild Oxidant

Testing with water-soluble mild oxidants (sodium perborate and hydrogen peroxide) was much less effective than testing with sodium permanganate. These tests led to high foam generation, which would make the mild oxidant hard to process in Tank 48H. The picture below (Figure 7.3.3.2) shows the foaming during testing with hydrogen peroxide. In addition, these tests resulted in much lower TPB decomposition than sodium permanganate (see Figure 3). The decomposition rate of these oxidants proved approximately equal to that of the blanks, experiments conducted without the addition of extra chemicals (i.e., no oxidants, no acid, and no catalyst). There was virtually no difference between the low peroxide addition and the high peroxide addition. This suggests that the peroxide reacted with itself and sodium hydroxide instead of TPB leading to little decomposition. However testing with Fenton's Reagent (hydrogen peroxide with iron catalyst) was very successful in destroying TPB with the addition of sufficient acid to reduce the solution pH to 9.5 (see Figure 4).

<sup>&</sup>lt;sup>3</sup> 4PB means 4 phenyl groups, 3PB means 3, 2 PB means 2, and 1PB is one phenyl group.



Figure 4 - Foaming produced during peroxide addition to Unwashed Precipitate

#### **Acid Hydrolysis Options**

The reference flowsheet for the destruction of TPB uses formic acid for hydrolysis of TPB. Several acids were investigated to determine whether formic acid is the best reagent for this process. Oxalic and nitric acid were tested in addition to formic acid. The advantage to these acids is that they all will decompose in the melter/offgas system and will not produce more glass in DWPF. In addition, they are not particularly corrosive to the DWPF process (although any acid will be corrosive in the carbon steel waste tanks if the solution pH is low enough). Oxalic acid has a low solubility in water (~8 wt %) so it would not be practical to lower the pH down 9.5 through the addition of >750,000 gallons of water. Many strong acids – including HCl, HF, and H<sub>2</sub>SO<sub>4</sub> – were rejected as they would be too corrosive or cause other problems such as glass solubility in the downstream processing. Also, the decomposition of TPB through acid hydrolysis is likely to produce benzene, which may lead to flammability issues.

#### **Nitric Acid**

Nitric acid was the most effective of the three acids tested, leading to complete destruction of the TPB via the addition of 4.1 moles of acid per mole of TPB. Formic acid was nearly as effective and produced fewer tar-like organics as judged by visual inspection. Based on the semi-volative organic analysis, twice as many aromatic compounds, 16 in total, were detected in the experiment with nitric acid than were detected in the

formic acid run. Many of these additional compounds were nitrated organics. Oxalic acid was not as effective as nitric or formic acid in our testing at 25 °C or 40 °C but was equally effective at 90 °C. Acids were very effective in destroying TPB but are not deployable as in-tank solutions as they would likely lead to excessive tank corrosion. Figure 4 and Figure 3 summarize the results of this testing.

An organic carbon mass balance was performed to understand the degree of TPB decomposition and the byproducts formed during decomposition. The HPLC analysis of the decomposition products showed that all of the TPB decomposed, primarily to 1PB. Based on the carbon balance, 8.2% of the original organic carbon converted to 1PB from the experiment using 4.1 moles of nitric acid per mole of TPB. If all of the TPB had decomposed to 1PB and stopped, there would be 25% of original carbon still present. This means that roughly two-thirds of the 1PB decomposed to benzene or another decomposition product. The data is summarized in Table 1.

Table 2 - Carbon Balance - %C based on HPLC analysis of selected samples

Description of Experiment	4PB	3PB	2PB	1PB	Others
5 moles NaMnO4 per mole TPB	88.28%	4.77%	4.23%	0.28%	52.00%
5 moles NaMn04 per mole TPB	5.28%	0.05%	0.19%	12.67%	8.08%
4.1 moles Formic Acid per mole TPB	0.04%	0.05%	0.04%	8.12%	1.59%
4.1 moles Nitric Acid per mole TPB	0.04%	0.05%	0.04%	14.06%	8.68%
1000 ppm Cu + 4.1 moles Formic Acid	0.04%	0.05%	0.04%	14.06%	8.68%
per mole TPB					

Nitric acid proved very effective in decomposing the TPB within the seven day testing period. Nitric acid led to 100% decomposition, as measured by soluble K, at both 25 °C and 40 °C. The disadvantage of this testing is that it led to a final pH of approximately 1, which would lead to increased tank corrosion. This alternative is viable, but is most likely to be successful in a separate processing tank rather than in Tank 48H.

#### Formic Acid

Formic acid was the second most effective of the three acids tested, leading to complete destruction of the TPB, as measured by soluble K, via the addition of 4.1 moles of acid per mole of TPB at 40 °C. As was mentioned above, formic acid produced fewer tar-like organics than nitric acid.

An organic carbon mass balance was performed to understand the degree of TPB decomposition and the byproducts that formed during decomposition. The HPLC analysis of the decomposition products showed that all of the TPB decomposed, primarily to 1PB. Based on the carbon balance, 14.1% of the original organic carbon was present as 1PB. If all of the TPB had decomposed to 1PB and stopped, there would be 25% of original carbon still present. This means that roughly 56% of the PBA decomposed to benzene or another decomposition product not measured by HPLC. The data is summarized in Table 2.

Formic acid was very effective in decomposing the TPB within the seven day testing period. Formic acid led to 84% decomposition at 25 °C and 100% decomposition at 40 °C. The disadvantage of this testing is that it led to a final pH of approximately 5, which would lead to excessive tank corrosion. This alternative is viable, but is most likely to be successful in a separate processing tank rather than in Tank 48H.

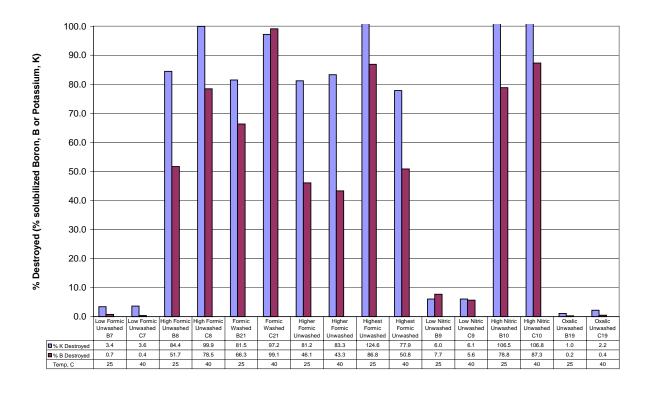


Figure 5-- Comparison of Acids for TPB Destruction

#### Fenton's Reagent

The addition of hydrogen peroxide with an iron catalyst (i.e., Fenton's reagent) proved effective in destroying the TPB in all the experiments (see Figure 6). The experiments used two concentrations of iron catalyst and the destruction was complete at both levels at 40 °C. Testing should be completed at lower concentrations so that the minimum amount of iron will be added. The testing was more effective at 40 °C but still destroyed 70% of the TPB at 25 °C in the seven days of testing. The final pH of all the solutions were much lower than planned. The final pH of the unwashed runs was approximately 5 (pH 9.5 was the target) due to over adding acid.

The recipe used in this experiment would result in the addition of 110,000 liters (30,000 gallons) of 90 wt % formic acid, 41,000 kg (92,000 lb) or 41,000 liters (11,000 gallons) of 30 wt % hydrogen peroxide, and 4500 kg (10,000 lb) of ferric nitrate. The advantage of using Fenton's reagent is that it will result in the addition of iron hydroxide and water (i.e., the hydrogen peroxide will decompose to water) to the HLW. The quantity of  $Fe_2O_3$  that would result from the addition of five moles of hydrogen peroxide per mole of TPB (57,600 kg or 127,000 lb) would lead to the addition of 900 kg (2,000 lb) of  $Fe_2O_3$  to the HLW.

Future testing should examine decreasing acid addition to determine if the reaction is effective at a higher pH.

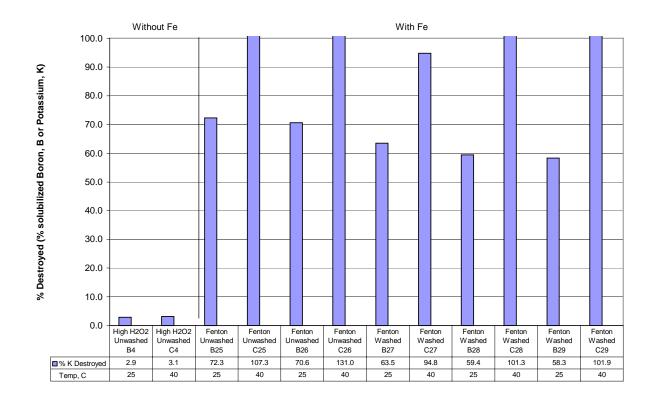


Figure 6- Comparison of Fenton's Reagent for TPB Destruction

#### **Acid Plus Permanganate**

The addition of sodium permanganate proved effective in partially destroying the TPB. The combination of acid and permanganate is often used to destroy organics. The combination of phosphoric acid and potassium permanganate is used in the Containment Facility in the Savannah River Technology Center's Shielded Cell Facility to destroy TPB. We examined whether TPB could be completely destroyed using a combination of sodium permanganate plus acid. Two experiments used this combination. Figure 7 summarizes the results. The combination led to approximately a five-fold increase in TPB decomposition (100%) compared to experiments using only permanganate.

The recipe used in this experiment would result in the addition of 1.1 million liters (30,000 gallons) of 90wt % formic acid and 57,600 kg (127,000 lb) of NaMnO<sub>4</sub>.

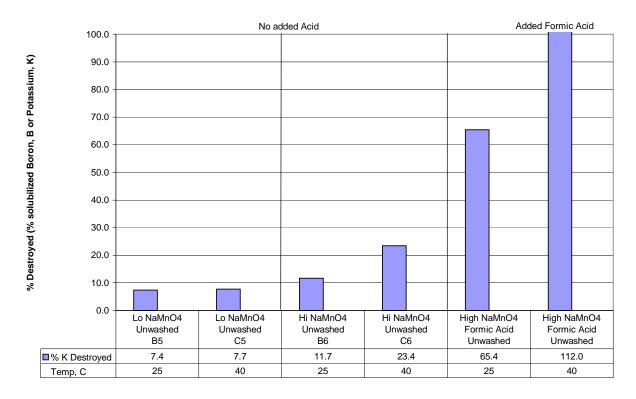


Figure 7 -- Comparison of Permanganate with and without Added Formic Acid for TPB Destruction

### **Summary**

The testing identified several new processes that should be considered as potential in-tank and out of tank processing options. The most promising options are listed below:

- 1. Fenton's Reagent at pH 3-5. This reaction led to 63% destruction of the TPB in the four day test with minimal byproducts (lowest production of organic in slurry and deposits of all six experiments) and lower production of benzene.
- 2. Permanganate at pH 3-5. This reaction led to 60% destruction of the TPB in the four day test with minimal byproducts and lower production of benzene.
- 3. Acid Hydrolysis (pH 3). This reaction led to 42% destruction of the TPB in the four day test. However, it had the highest production of benzene.
- 4. Fenton's Reagent at pH >9. This reaction led to 36% destruction of the TPB in the four day test with minimal byproducts and lower production of benzene.

The Tank 48H Team recommended continuing experiments to assess the viability of oxidation, catalyst and acidic processes and the use of sodium permanganate and Fenton's reagent to oxidize the TPB be developed as possible in-tank alternatives.

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